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THE EFFECT OF UNDERPRESSURE ON GAS RELEASE PROCESSES IN FIRING CLAY

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It is found that when clays are fired at underpressure, the reactions with the formation of volatile components proceed at a lower temperature, and the gaseous medium is reducing. At the same time, the sintering mechanism is modified, and the physicomechanical properties of the products obtained improve.

The ceramic technology processes that take place in firing and involve the releasing of gaseous materials are not sufficiently studied. This is due not only to the existing opinion on a little significance of gases release from argillaceous rocks, but also to the difficulty of setting experiments.

A. S. Sadunas with colleagues in their research established that gases released from clay have nearly no effect on the composition of the gaseous medium of the firing zone [1].

A. V. Nekhoroshev in [2] demonstrated that the process of gas release can be regulated by varying the rate and duration of heating or by water steam that increases the activity of the gaseous components.

Nevertheless, neither the specified studies, nor others [3, 4] consider certain aspects of the reactions with the participation of gaseous products. In particular, little attention is paid to the role of carbon, which, being the product of decomposition of organic compounds, with a further increase in temperature becomes oxidized and modifies the composition of the gaseous medium. The effect of variable-valence compounds contained in clays, which become transformed into their active forms via gaseous reactants and produce other volatile components, is not sufficiently investigated either. The only technological parameters that have been used to control the gas release processes are the temperature and pressure of the vapor-gaseous medium.

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In this context the gas formation sources and the composition and the type of the gas medium in firing argillaceous rocks with different chemicomineralogical bases are of theoretical interest, and the development of new techniques makes it possible to control the gas release processes in practice, in order to obtain ceramic products with preset properties.

The present study considers the quantitative and qualitative composition of gases released in heat treatment of argillaceous materials, while varying one of the technological parameters, i.e., decreasing the gas medium pressure in the firing zone to accelerate the processes of releasing gas reactants.

For our study we selected low-melting Sheminskoe and Ongar-Khovunskoe clays from the Republic of Tuva. The Sheminskoe clay has a hydromica base and the Ongar-Khovunskoe clay has a montmorillonite base. Table 1 lists the composition of the initial clays.

The following method was used in research. Cylindrical samples of diameter and height 10 mm were molded from milled and dried clay by dry molding at a unit pressure of 100 MPa. The thermal treatment was performed in a quartz tube of diameter 25 and length 200 mm at underpressure of 133 – 532 Pa. The tube was placed into a laboratory microelectric furnace connected with a MX-1323 mass spectrometer. In firing, a gas flow is supplied into a special chamber of the mass spectrometer where it is subjected to ionization in

TABLE 1

Clay	Mass content, %									
	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	calcination loss
Sheminskoe	61.22	17.24	0.93	7.68	1.60	2.58	2.16	1.55	0.08	4.65
Ongar-Khovunskoe	55.15	16.48	0.89	5.01	5.54	2.90	2.18	1.24	0.64	9.62

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TABLE 2

Clay	Firing temperature, °C	Gas content, vol.%					
		H_2	CO	CO_2	O_2	N_2	CH_4
Sheminskoe	250	4.16	30.48	23.35	6.25	44.37	0.39
	350	6.24	34.05	18.70	4.17	36.10	0.35
	550	10.17	38.28	30.18	0.48	20.04	0.28
	750	11.29	49.50	32.41	0.62	7.23	0.25
	950	18.64	21.17	57.96	0.94	0.41	0.21
Ongar-Khovunskoe	300	4.92	58.80	15.90	3.80	15.60	0.65
	550	3.52	53.00	25.60	0.58	10.25	0.23
	750	9.10	26.20	61.40	0.70	2.60	0.14
	950	24.12	17.16	56.13	0.58	1.24	0.11

vacuum at a pressure of 10^{-5} Pa. The strength of current in studying components with different masses is the measure of the content of the particular component in the analyzed glass. The gas analysis was performed within the temperature range in which the main physicochemical processes releasing gas components take place.

The content of organic compounds in clays was determined using a Lekko set (USA). The volatile firing products (CO and CO_2) were analyzed on molecular sieves. Next, based on the results of the volume content of the specified gases, the content of dry carbon in them was calculated. The content of organic compounds in the Sheminskoe and Ongar-Khovunskoe clays converted to dry carbon was 0.84 and 0.88%, respectively.

The iron-bearing minerals in argillaceous rocks and their subsequent phase transformations in firing were determined using the Mossbauer spectroscopy method (nuclear gamma-resonance spectroscopy, NGRS).

The results of the gas analysis are shown in Table 2. The analysis of the obtained data indicates that the intense decomposition of organic compounds accompanied by the release of hydrogen, carbon monoxide, and carbon dioxide takes place in the temperature interval of 200 – 300°C. Sheminskoe clay in this case releases 30.48% CO and 4.16% H_2. The gas medium already at this stage is reducing. A reducing gas medium is created with over 6% hydrogen and carbon monoxide in the gas mixture [1]. Along with the specified gases, up to 23.35% carbon dioxide is registered in the gas medium. These data well agree with the opinion of G. L. Stadnikov [5] that in clay heating, humin acids split part of carboxyls leading to the formation of CO and CO_2.

The development of underpressure in the firing zone substantially accelerates the pyrogenetic decomposition of organic compounds and the formation of physically bonded water. The quantity of the gaseous and vapor phases released can be estimated based on the weight variations of the sample fired. The study of weight losses (Table 3) indicated that Sheminskoe clays samples under heat treatment up to 250°C at underpressure lose up to 3.0 wt.% and in normal condition around 1.9 wt.%. Furthermore, due to the decomposition of organic compounds, the carbon content in Sheminskoe clay decreases to 0.68% (Table 4).

In the temperature interval of 300 – 550°C the formation of active gases (H_2 and CO) intensifies and reaches 48%. Simultaneously, the content of carbon dioxide grows. This is related to the reactions of the oxidation of carbon, whose content gradually decreases. Despite the reducing type of the gaseous medium, the residual oxygen content (3 – 4%) facilitates a further oxidation of carbon. Another essential factor is the fact that the intense dehydration of argillaceous minerals at underpressure starts at a temperature of 400°C (Table 3). Later the gas medium becomes enriched with reducing gases due to carbon residue and constitution water. As a result, the quantity of residual carbon in Sheminskoe clay decreases to less than one third, i.e., from 0.59 to 0.18% (at the temperatures of 350 and 550°C, respectively).

At 300 – 550°C the ferrous compounds contained in the clay become involved in the processes leading to the formation of volatile components. It was earlier [5] found using the NGRS method that in firing low-melting Tuva clays at underpressure at a temperature exceeding 350°C, magnetite and wustite are registered along with α-Fe_2O_3. The various forms of iron oxides in this case are formed with the participation and formation of the following gas reactants:

$$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2;$$

$$Fe_3O_4 + CO = 3FeO + CO_2.$$

The analysis of the above reactions shows that the phase transformations of iron oxides agree well with the results of the gas analysis. The reduction of magnetite and wustite by carbon monoxide is corroborated by the increasing content of carbon dioxide in the gaseous medium.

With a further increase in temperature (from 550 to 750°C), the increasing content of wustite is related to hydro-

TABLE 3

Sample	Firing temperature, °C	Weight loss, %	
		underpressure*	normal pressure
1	100	0.2	0.0
2	200	1.8	1.2
3	250	3.0	1.9
4	300	3.2	2.8
5	400	3.3	3.0
6	500	5.1	3.2
7	600	6.7	4.3
8	700	7.4	6.0
9	800	7.7	6.4
10	900	7.9	6.6
11	1000	8.0	6.8

* 133 – 532 Pa.

TABLE 4

Firing temperature, °C	Mass content of carbon, %	
	Sheminskoe clay	Ongar-Khovunskoe clay
20	0.84	0.88
150	0.78	0.82
250	0.68	0.70
350	0.59	0.58
450	0.40	0.41
550	0.18	0.20
650	0.08	0.09
750	0.06	0.07
850	0.05	0.06
950	0.04	0.05

gen accumulated in the inner layers of the heat-treated material:

$$Fe_2O_3 + H_2 = 2FeO + H_2O.$$

Another reactant facilitating the formation of wustite in the specified temperature interval is carbon in the form of a solid residue:

$$Fe_2O + C \rightarrow FeO + CO.$$

Precisely within this interval the formation of carbon monoxide from the Sheminskoe clay is registered up to 49%. Furthermore, an increase in the content of carbon monoxide (up to 61% for the Ongar-Khovunskoe clay) continues, which depends on the early start of the decomposition of carbonates due to a decreased pressure of the medium in firing. The reactions with the participation of carbon ends at a temperature of 750°C, which is evidenced by a substantial decrease of the latter component.

In the temperature range of 800 – 950°C, the concentration of hydrogen in the gaseous medium increases (up to 18 and 24%), which is due to the pyrolysis of the constitution water molecules at underpressure. An increase in the content of CO_2 can be attributed to the reduction of wustite according to the reaction:

$$Fe_3O_4 + CO = 3FeO + CO_2$$

with the formation of carbonic acid and continuing dissociation of carbonates. It is established [6] that a highly reducing gas medium facilitates the transition of up to 85% iron oxide into its more active form. Wustite, which has the most active reaction capacity among all ferrous compounds, intensifies the sintering of clay mixtures and participates in the formation of a liquid phase at earlier stages of firing.

Consequently, the decreased pressure in the firing zone modifies the kinetics of the gas release processes, As a consequence of firing at underpressure, ceramic materials released more gaseous products than under normal pressure. At underpressure the gas medium remains reducing during the entire firing process. Therefore, the ceramic material fired in these conditions has improved properties.

Table 5 gives the physicomechanical properties of heat-treated samples of Sheminskoe clay. These results indicate an earlier start of sintering in Sheminskoe clay under a decreased pressure in a reducing medium (compared to the standard firing procedure at 100°C). The samples fired at 900°C at underpressure have volume shrinkage 3.8% and strength 57.1 MPa. Approximately identical parameters are registered in the samples fired at 1000°C under normal pressure.

The underpressure and the reducing gaseous medium in firing modify the sintering mechanism of argillaceous mixtures. First, a decreased partial pressure of the gaseous components shifts the beginning of the chemical reactions toward lower temperatures. Second, the removal of the gaseous products from the material fired is more intense due to the pressure difference, which substantially increases the effect of the volatile components on the sintering process, eliminates the possibility of their explosive release, and facilitates closer contacts between solid particles. Third, the reducing gas medium results in the fact that ferrous compounds transform into more active forms (wustite and spinels) and form low-temperature melts.

A vacuum electric furnace was constructed to verify the experimental data. As a consequence of firing of a prototype brick batch made by semidry molding in underpressure (133 – 399 Pa) and fired at a temperature of 980°C, ceramic facing brick of grades M150 – M200 with water absorption 7.2% was obtained. (under normal pressure bricks with water absorption below 8% were produced after firing at 1060°C). Furthermore, firing at underpressure substantial expands the sintering interval for low-melting clays. The firing duration is this case decreases substantially (by half or to one-third).

TABLE 5

Sample	Firing temperature, °C	Underpressure*				Normal pressure			
		mean density, g/cm^3	volume shrinkage, %	water absorption, %	compression strength, MPa	mean density, g/cm^3	volume shrinkage, %	water absorption, %	compression strength, MPa
1	700	1.92	1.1	16.8	27.0	1.90	0.7	18.2	22.3
2	800	1.96	2.7	14.1	38.5	1.93	1.6	16.9	29.5
3	900	2.02	3.8	10.9	57.1	1.97	2.9	13.9	40.7
4	1000	2.12	5.9	6.8	72.6	2.04	4.0	10.1	58.7
5	1100	2.00		Deformation		2.14	6.1	6.4	74.1

* 133 – 532 Pa.

Thus, gaseous products are released from a clay mixture more intensely under a decreased pressure and determine the type of the gas medium and, accordingly, contribute to improving the quality of ceramic products.

REFERENCES

1. A. I. Sadunas and S. S. Norkute, “The role of gases released from clay in the development of media for firing ceramic materials,” in: *Redox Processes in Silicate Systems, Proc. Scient. Tech. Conf.* [in Russian], Vilnius (1969), pp. 74 – 75.
2. A. V. Nekhoroshev, *Theoretical Principles of the Technology of Thermal Treatment of Inorganic Building Materials* [in Russian], Stroiizdat, Moscow (1978).
3. S. P. Onatskii, *Production of Claydite* [in Russian], Stroiizdat, Moscow (1987).
4. M. I. Rogovoi, *Technology of Synthesized Porous Fillers and Ceramics* [in Russian], Stroiizdat, Moscow (1974).
5. G. L. Stadnikov, *Origin of Clays and Coals* [in Russian], Izd-vo Akad. Nauk SSSR, Moscow (1957).
6. B. K. Kara-sal, “Intensification of sintering of argillaceous rocks with a high content of iron by modifying the parameters of the firing medium,” *Izv. Vuzov, Ser. Stroitel’stvo*, No. 10, 43 – 48 (2003).